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Compressibility, free length, molar and available volume in ternary liquid mixtures

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Adiabatic compressibility, free length, molar volume and available volume have been evaluated from density and ultrasound velocity measurements in four ternary liquid mixtures.

1. Introduction

Ultrasonic study of molecular interaction in binary liquid mixtures has been made by several workers such as Moelwyn-Hughes & Thorpe (1964), Rao & Rao (1965), Fort & Moore (1965), Snyder & Snyder (1974), Prakash *et al* (1975) and many others. However, not much has been done in ternary and quarternary liquid mixtures. Slaszka (1971) and Prakash *et al* (1972) have reported their results in ternary mixtures, while Nozdrev & Yashina (1965) tried a quarternary system.

In the present communication we have dealt with four ternary liquid mixtures with regard to the various physical parameters, viz., adiabatic compressibility (β), intermolecular free length (L_f) molar volume (V) and available volume (V_a) obtained from the ultrasound velocity (v) and density (ρ) data in methanol-chlorobenzene-carbontetrachloride (I), acetone-toluene-chloroform (II), *n*-heptane-benzene-carbon tetrachloride (III) and *n*-hexane-benzene-butanol (IV). The purpose was to study the acoustic and physicochemical behaviour of a mixture of liquids consisting of three components in which interactions between two are already known to be occurring. Free length L_f was calculated with the help of Jacobson's (1952) relation

$$L_f = K\sqrt{\beta} \qquad \ldots (1)$$

where K is the temperature dependent constant and β is the adiabatic compressibility obtainable from $\beta = \frac{1}{v^2\rho}$, where v is the ultrasound velocity and ρ is the density of the medium.

Available volume is given in terms of geometrical volume (B), the collision factor (S)and the molar volume (V) as

$$V_a = V - SB \qquad \ldots (2)$$

Table 1. Ultrasound velocity and related parameters in the system methanol+chlorobenzene+carbontetrachloride at 23°C

Mole fraction of chloro benzene	Mole fraction of carbon tetra-chloride	v m/s	ρ gm/cm^3	$\beta \times 10^{12}$ (exptl) cm^2/dyne	Lf (exptl) Å	V (exptl) ml/mole	Va (exptl) ml/mole
0.00	0.60	940	1.4190	79.8	0.556	74.1	30.5
.010	0.50	983	1.3550	76.3	0.544	74.5	28.7
0.20	0.40	1030	1.2920	72.9	0.531	74.9	26.7
0.30	0.30	1076	1.2280	70.3	0.521	75.5	24.7
0.40	0.20	1132	1.1620	67.0	0.509	76.0	22.2
0.50	0.10	1191	1.1040	64.0	0.498	76.6	19.6
0.60	0.00	1247	1.0420	61.8	0.489	77.1	17.0
0.50	0.50	1100	1.3420	61.6	0.488	99.3	31.0
0.00	0.00	1133	0.7903	98.6	0.618	40.5	11.8
1.00	0.00	1304	1.1020	53.4	0.455	102.2	18.9
0.00	1.00	928	1.5830	73.3	0.533	97.2	40.8

Table 2. Ultrasound velocity and related parameters in the system acetone+toluenechloroform at 23°C

Mole fraction of chloro-form	Mole fraction of toluene	v m/s	ρ gm/cm^3	$\beta \times 10^{12}$ (exptl) cm^2/dyne	Lf (exptl) Å	V (Exptl) ml/mole	Va (exptl) ml/mole
0.00	0.60	1296	0.8410	70.8	0.523	93.4	17.7
0.10	0.50	1242	0.8950	72.4	0.529	90.8	20.3
0.20	0.40	1194	0.9519	73.7	0.534	88.2	22.4
0.30	0.30	1145	1.0180	74.9	0.538	85.1	24.2
0.40	0.20	1108	1.0830	75.2	0.539	82.5	25.4
0.50	0.10	1074	1.1490	75.4	0.540	80.2	26.4
0.60	0.00	1034	1.2180	76.8	0.545	77.9	27.5
0.50	0.50	1141	1.1260	68.2	0.514	93.9	26.9
0.00	0.00	1200	0.7861	88.3	0.585	73.9	18.5
1.00	0.00	1002	1.4690	67.8	0.512	81.3	30.4
0.00	1.00	1320	0.8612	66.6	0.508	107.0	18.7

Table 3. Ultrasound velocity and related parameters in the system heptane+benzene+carbon—tetra+chloride at 23°C

Mole fraction of benzene	Mole fraction of carbon tetra-chloride	v m/s	ρ gm/cm³	$\beta \times 10^{12}$ (exptl) cm²/dyne	Lf (exptl) Å	V (exptl) ml/mole	Va (exptl) ml/mole
0.00	0.60	988	1.1230	91.3	0.594	118.0	45.2
0.10	0.50	1016	1.0651	90.9	0.593	117.2	42.8
0.20	0.40	1052	1.0070	89.8	0.589	116.5	39.9
0.30	0.30	1089	0.9477	88.9	0.587	115.8	36.9
0.40	0.20	1131	0.8874	88.0	0.584	115.0	33.7
0.50	0.10	1179	0.8271	87.1	0.581	114.2	30.1
0.60	0.00	1230	0.7674	86.1	0.577	113.3	26.2
0.50	0.50	1064	1.2430	71.0	0.524	93.4	31.3
0.00	0.00	1065	0.6789	108.5	0.648	147.6	40.1
1.00	0.00	1310	0.8732	66.7	0.508	89.5	16.2
0.00	1.00	928	1.5830	73.3	0.533	97.2	40.8

Table 4. Ultrasound velocity and related parameters in the system n-hexane+benzene+n-butanol at 23°C

Mole fraction of n-butanol	Mole fraction of benzene	v m/s	ρ gm/cm³	$\beta \times 10^{12}$ (exptl) cm²/dyne	Lf (exptl) Å	V (exptl) ml/mole	Va (exptl) ml/mole
0.20	0.50	1227	0.7741	85.5	0.575	103.0	24.0
0.30	0.40	1227	0.7688	86.4	0.578	103.2	24.1
0.40	0.30	1226	0.7638	87.1	0.580	103.4	24.2
0.50	0.20	1223	0.7586	88.2	0.584	103.5	24.4
0.70	0.00	1230	0.7499	88.1	0.583	103.6	23.9
0.60	0.20	1243	0.7773	83.3	0.568	99.4	22.2
0.50	0.50	1289	0.8371	71.9	0.527	90.9	17.7
0.00	0.00	1113	0.6580	122.7	0.689	131.0	39.9
1.00	0.00	1315	0.8076	71.6	0.526	91.8	16.4
0.00	1.00	1310	0.8732	66.6	0.508	89.5	16.2

where S could be eliminated with the help of Schaaff's expression (1939) for velocity of sound in liquids i.e. $v = v_\infty \frac{SB}{V}$, where $v_\infty = 1600 m/s$ and hence eq. (2) could be reduced to

$$Va = V\left(1 - \frac{v}{v_\infty}\right) \qquad \ldots (3)$$

Eq (3) has been used to evaluate Va values.

2. Experimental

Ultrasound velocity at the frequency of 5 Mc/S was measured by the light diffraction method. The source of ultrasound waves was a generator comprising an oscillator unit and a gold plated quartz crystal 2.54 cm. in diameter as transducer. An optical cell suitably designed by Prakash & Prakash (1966) was used for containing the solution and with the help of a filter light of wavelength 3656°Å from a mercury vapour lamp was allowed to fall normally to the path of ultrasonic waves. Such waves traversing in a liquid set-up a periodical inhomogeneity which acts as an optical grating. The diffraction patterns were photographed on orthochromatic Agfa Plates and fringe distances were measured by a comparator fitted with a travelling microscope and vernier scale reading upto 0.0001 cm. The liquids used were AR(BDH) grade and were distilled and purified by standard methods. The densities were determined using double walled pyknometer having capillaries of narrow bore provided with well fitting glass caps in order to avoid changes in the composition because of evaporation of more volatile component. The pyknometer was calibrated with distilled water and pure benzene. The temperature was controlled to ± 0.1°C by using the thermostat with electronic relay system. The accuracy of density is 1 in 10^4 and that of ultrasound velocity is 0.20 per cent.

3. Results

The results of ultrasound velocity, adiabatic compressibility, intermolecular free length, molar volume and available volume have been presented in tables 1-4. A perusal of the tables clearly demonstrates how these properties vary with the change in composition of the system.

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